

Composite Sn-based Anodes with Improved Cycle Life

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Introduction

The development of alternative anodes for Li ion batteries such as those based on metal alloys, e.g. Li-Sn, provides an opportunity to improve the capacity of these batteries. Metallic Sn can alloy up to 4.4 Li per Sn atom, corresponding to a capacity of 992 mAh/g, more than two times the theoretical capacity of graphite (372 mAh/g). One drawback of these materials is the significant expansion that occurs in the Sn host during Li alloying (260%). The repeated expansion/contraction of the lattice during cycling degrades the Sn structure, severely limiting cycle life. Several strategies to improve cycle life have been reported including tin oxide-based glasses, tin-metal alloys, and Sn-based composites, but none have succeeded in producing a commercially viable material.

T/J Technologies recently reported the synthesis and characterization of a new type of anode material based on composites of nanoscale metallic Sn domains embedded in a transition metal carbide (TMC) host.[1] The high capacity of Sn combined with the excellent electronic conductivity and thermal stability of the TMC host produces electrode materials that exhibit high reversible capacity (up to 500 mAh/g), high first cycle reversibility (up to 91%), excellent rate capability (84% full capacity at 2C for 100% depth of discharge), and moderate cycle life (up to 25). This report describes a chemically modified version of these nanocomposite materials significantly improves cycle life.

Experimental

The Sn-based nanocomposite materials were prepared via two routes: high temperature chemical reduction and high impact ball milling (HIBM). The modified versions of these materials were produced using similar methods, but included a chemical dopant in the synthesis. The capacity of the materials was controlled by the relative ratio of Sn:transition metal. Crystallographic and microstructural analysis was performed on the composite samples using x-ray diffraction and SEM.

Electrodes of the composite materials were prepared using 5 wt.% conductive carbon and 8-15 wt.% polyvinylidene fluoride (PVDF) binder dissolved in n-methylpyrrolidinone (NMP). Button cells were fabricated in a glove box using the Sn/TMC composites as the positive electrode, and Li metal foil as the negative electrode. The separator was Celgard 3501, and the electrolyte was 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate (2:1) solvent. Cells were tested on a Maccor Series 4000 24 channel battery tester.

Results and Discussion

The objective of this study was to improve the cycle life of the T/J nanocomposite materials through rational materials design. Chemical doping of the Sn /TMC nanocomposite materials during processing produced materials that showed significantly improved cycle life (>100) while maintaining a high capacity (up to 250 mAh/g) and a high first cycle reversibility (>70%). Figure 1 shows a comparison of the charge and discharge capacities (recorded at C/2) for a doped Sn/TMC composite versus an non-doped Sn/TMC composite

sample versus cycle number. The initial capacity of the doped material is reduced relative to the standard Sn/TMC composite, but the extended cycling shows significantly improved behavior. A second salient feature in Figure 1 is the substantially improved the coulombic efficiency of the doped material during charge/discharge. The coulombic efficiency of alternative Sn-based anode materials has typically been unsuitable for use in Li ion cells due to the accumulated charge loss versus time. We achieved greater than 99.5% efficiency for each charge/discharge cycle while cycling compared to ~95% for the non-doped materials.

A comparison of the voltage versus time profile for the doped and non-doped Sn-based composites is shown in Figure 2. The sloping discharge curve of the doped materials indicates that the material is not undergoing distinct phase transformations as was observed for the non-doped materials. The dramatic change in the voltage profile of the doped materials can be attributed in part to reduced Sn crystallite size within the material.

In this presentation, the influence of composition and microstructure on the performance of these new materials will be discussed.

Acknowledgements

The authors gratefully acknowledge the National Institute of Standards and Technology (NIST) and the Advanced Technology Program (ATP) for support.

[1] Wang, L., Fay, M., Miller, J., Glomski, B., Wrosch, M., Wixom, M., and Thompson, L., in Proceedings of the 39th Power Sources Conference, June 12-15, 2000, Cherry Hill, NJ, pg. 85.

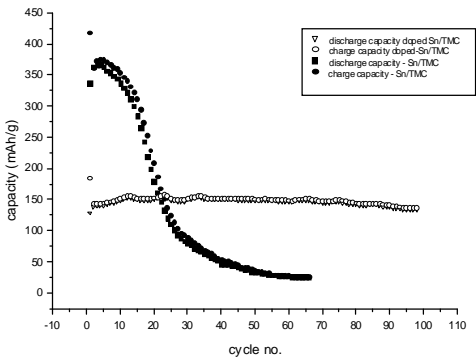


Figure 1. Comparison of capacity versus cycle life for doped and undoped Sn/TMC composite anode materials.

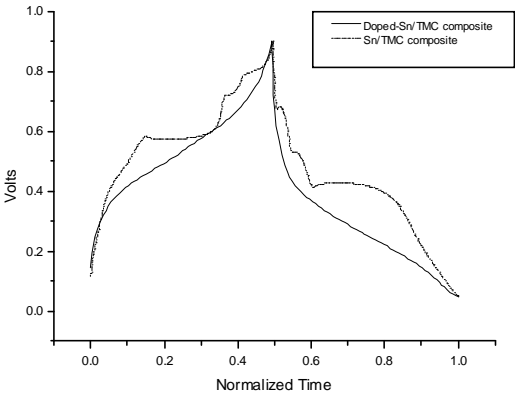


Figure 2. Comparison of Voltage versus time profiles for doped and undoped Sn/TMC composite anode materials.